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Laboratory for Physical Science  
P. R. Mallory & Co. Inc.  
Northwest Industrial Park  
Burlington, Massachusetts

Technical Management  
NASA - Lewis Research Center  
Space Electric Power Office  
Attention: Mr. Daniel G. Soltis

Third Quarterly Report for Research  
& Development of a High Capacity  
Non-Aqueous Secondary Battery

Contract Number NAS3 - 2780

Submitted by:

P. R. Mallory & Co. Inc.  
Laboratory for Physical Science  
Northwest Industrial Park  
Burlington, Massachusetts  
Tel. No. 617-272-4100

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## SUMMARY

During this quarter most of our investigations have been conducted in electrolytes employing a propylene carbonate solvent. The problems which we have studied are related to the basic electrode behavior and to the solute; the solvent seems less important. A solution to these problems is essential before a satisfactory high energy density non-aqueous battery can be developed.

1. Lithium, the most desirable high energy density anode, exhibits completely satisfactory behavior insofar as the current efficiency for deposition is concerned and the metal deposit appears to be chemically stable in propylene carbonate solutions. The nature of the deposit, however, is unsatisfactory with respect to succeeding re-anodization efficiency. Improvements may be expected as more is known about the effects of the solute composition on deposition behavior.

2. The effect of electrolyte impurities may be severe. Decomposition impurities are introduced when solute is added to solvent. Even the small amount of water remaining after vacuum distillation may be deleterious. Progress has been made in assessing the damage resulting from the presence of these impurities, and in eliminating them. It is likely that major improvements will result from modifications in the entire procedure for synthesizing the complete solute-solvent system.

3. Iron, Cobalt, and nickel metals appear not to function satisfactorily in a cathode couple, since the reduction to the metal proceeds so irreversibly. It is likely that cathodes incorporating these elements as well as chromium and manganese will involve couples employing transformations between two higher valence states on charge-discharge cycling.

4. Silver is reversibly oxidized in chloride containing electrolytes on cathodization to an insoluble salt, which is completely recovered on subsequent anodization. It appears that all of the chloride in the electrolyte is available for combination with silver. This fact is rather surprising but appears to result in localized solvent decomposition at the electrode surface during anodic charging, and this may be deleterious on prolonged cycling.

5. Copper is reversibly oxidized to a salt in chloride and fluoride electrolytes. The salts are not satisfactorily insoluble, but improvements may be expected as a result of appropriate modifications in the composition of more complex solute systems.

## PART I. INTRODUCTION

In our work on the research and development of high energy density, secondary, non-aqueous batteries we have deliberately directed most of our attention toward phenomena occurring at the individual electrodes. We have been concerned with determining the extent to which standard electrometric techniques, performed under well-defined laboratory conditions, may yield useful information about the chemical and electrochemical processes occurring at the electrodes and within the electrolyte. We are particularly concerned that this information should be such as to suggest logical approaches toward improving the behavior of systems with respect to their ultimate incorporation in secondary cells. We anticipate a host of developmental problems will be encountered before a practical organic secondary battery is finally perfected; some will be similar to those arising in the development of aqueous batteries, others will be uniquely different, requiring the use of technologies previously untried in battery fabrication.

One cannot presume that, because an electrode-electrolyte system functions well under ideal laboratory conditions, equally good behavior will be exhibited when the basic system is incorporated in an actual battery. However, one can be quite sure that the developmental problems encountered in using an electrode-electrolyte system which does not function well under ideal conditions will increase at least proportionately with increasing deviation from ideal behavior.

The characteristics of a secondary battery are described in such terms as: "Depth of charge," "charge acceptance," "cycle life," "capacity," and "self-discharge." The range of operating conditions under which these properties may have satisfactory values is always limited by the nature of the detailed processes occurring at the battery electrodes, and knowledge of these processes is vital to the systematic improvement of cell performance. The possibility does indeed exist that electrode reactions may be tailored to specific applications as has been done in e.g. electroplating.

The procedure we have followed in our work is, in essence, to subject a system to chemical and electrochemical perturbations to obtain a clear pattern of behavior ascribable to the perturbation, from which one may deduce an adequate chemical and electrochemical model. The model, if adequate, will suggest logical procedures for improving the system under study and predict ultimate limitations to the utility of the system.

Chemical perturbations consist simply of the successive addition of increments of appropriate material to the solution. Since the composition of the diffusion layer differs during electrolysis from the composition of the bulk of solution the degree of mechanical agitation may be considered to be a chemical perturbation. Electrochemical perturbations are the current pulses of varying magnitude and duration applied to the working electrode.

One of the main difficulties in studying electrode behavior is that the variables accessible to accurate measurement -- current, potential, time, conductivity -- are relatively few and that electrodes and electrolytes are receptive to a host of other perturbations which are reflected in these variables. A large body of reliable and reproduceable data is required, therefore, which is collected under such conditions that the effect of unknown perturbations is constantly being probed. Only then can a self-consistent model be constructed of the system.

In our work we are examining not only phenomena but also techniques for studying these phenomena. We are of the opinion that both the phenomena and the techniques have general relevance to systems employing other than propylene carbonate. cursory examination of systems operating in acetonitrile, acetone, and butyrolactone has shown this to be true. For this reason, we have been somewhat reluctant to undertake extensive experiments in solvents other than propylene carbonate.

In this report we shall frequently refer to analogous behavior observed in aqueous systems, since an important part of the work in non-aqueous systems should be enunciation of those differences which do exist. The experimental techniques employed have been adequately discussed in previous reports but a brief discussion of this area is appended for clarity.



Three problem areas appear most critical: The deposition of lithium in suitable form, the detection and elimination of impurities, and the control of the solute equilibria to diminish the solubility of species formed on charge and discharge.

## PART II. THE LITHIUM ELECTRODE IN PROPYLENE CARBONATE

Introduction. We were concerned with studying in more detail the deposition behavior observed on reduction of lithium and the physical, chemical, and electrochemical properties of the lithium deposit so obtained. Such information has clear relevance to the incorporation of the electrode in a secondary battery but is also important in reflecting certain important properties of the electrolyte itself. The latter point cannot be overemphasized since the lack of knowledge which currently prevails concerning the role organic electrolyte systems play with respect to their influence on electrode behavior is reminiscent of the situation which prevailed with respect to aqueous solutions during the latter part of the last century.

In this section we shall separately discuss the electrodeposition behavior of lithium and the properties of the deposit.

Electrodeposition behavior of lithium. We are concerned whether the deposition of lithium from propylene carbonate solutions is well-behaved electrochemically, by which we specifically mean whether the limiting current (in either stirred or quiet solution) for lithium deposition is directly proportional to the lithium ion concentration in solution, and whether deposition proceeds with 100% current efficiency at currents below the limiting current. Neither statement implies the truth of the other as will be shown below.

For the electrolytic reduction of a soluble metal ion to the metal there exists a limiting current. This is defined as the maximum rate at which metal

ions in solution may be reduced to the metal, under steady state conditions. There is also a maximum rate at which metal ions can be supplied to the electrode surface. If all metal ions can be reduced immediately over all parts of the metal surface then the limiting current will be equal to the maximum rate at which ions can be supplied to the surface. In this case it is found that under ideal steady state conditions the limiting current is directly proportional to the electrode area and to the bulk concentration of metal ions. If some of the metal ions are not immediately reduceable, or some of the electrode surface is unavailable for reduction, then this proportionality will not be true. The polarographic literature is replete with cases where the limiting current is, in fact, not directly proportional to concentration and electrode area. A determination of the relationship between concentration and limiting current is one of the first steps in any electrochemical investigation.

The preceding discussion may imply that at currents below the limiting current metal deposition will proceed with 100% current efficiency, but this is not true. Suppose there exists in the solution a second species which is thermodynamically capable of reduction more easily than the metal ion. An example would be a solution of +2 lead and hydrogen ions. One would predict that in such a solution it would be impossible to reduce the metal without concurrent evolution of hydrogen gas. This is not the case, however, because the overvoltage for hydrogen reduction on lead is so large. However, since overvoltage decreases with decreasing current, one may envisage a situation

where the deposition of lead is attempted at such low currents that the resultant, very small, overvoltage for the reduction of hydrogen results in the production of more hydrogen gas than of metallic lead. This is a common situation -- two species are present (one may be solvent itself) whose kinetic activity is the reverse of the thermodynamic activity.

A plot of the current efficiency for lead deposition versus current density would show that, at very low current, efficiency is low, increasing at higher currents to close to 100%, and sharply decreasing at currents above the limiting current. It was our intention to obtain such a pattern of deposition behavior for the reduction of lithium in propylene carbonate solution.

We have found relatively little information in the literature on the deposition and re-anodization cycling of electrodes under well-controlled conditions. Since our previous experience in performing such experiments in aqueous solution had convinced us that the observed behavior is rarely as simple and clear-cut as theory would predict, we felt that this area of research would be particularly appropriate with respect to secondary battery electrodes.

We, therefore, began our investigations with the deposition and subsequent re-anodization of lithium from propylene carbonate solution. We were concerned not only with the behavior of the lithium electrode per se but also with the information such behavior might yield about the electrolyte itself. We were surprised to observe that the deposition behavior of lithium was quite well-behaved. It would have been naive to presume that such would be the case for such an active metal.

Following the earlier work of the Lockheed group we started our investigations with the  $\text{LiCl-AlCl}_3$  - propylene carbonate electrolyte. Electro-metric measurements were first made in solutions of  $\text{AlCl}_3$  alone, followed by a series of measurement made after the successive incremental additions of  $\text{LiCl}$ . The results of this work have been reported in our earlier reports, however, further experiments during this quarter have somewhat modified our original interpretation.

When  $\text{AlCl}_3$  alone is added to propylene carbonate, a vigorous heat of solution is attended with the development of a deep golden-brown color. In Figure 1 are shown a series of chronopotentiograms obtained in a propylene carbonate solution, 0.35 M in  $\text{AlCl}_3$ . Two questions of concern involve the significance of the potential of the initial plateau, and the cause of the potential break at the transition time.

We have made no attempt as yet to measure potentials with a well-defined reference electrode, nor any attempt to minimize  $iR$  drop through establishing electrical contact between both electrodes via a Luggin capillary. The reference electrode is simply a silver disc imbedded in epoxy resin about a centimeter from the working electrode disc. Thus the measured potential of the working electrode with respect to the reference includes a sizable  $iR$  drop, and this unquestionably accounts for the high potential exhibited during the initial plateau.

If the material being consumed during reduction is charged, the depletion of charged species in the diffusion layer will markedly increase the resistance of the diffusion layer towards the end of reduction. The large change in potential at the transition time doubtless reflects almost total depletion of conducting material in the diffusion layer. This type of behavior is not normally observed in aqueous electrolysis. The closest analogy to aqueous electrode behavior is that observed when a valve metal -- aluminum or tantalum -- is anodically oxidized to an insulating oxide. As the film grows linearly with time (at constant current), the resistance of the film increases proportionately. The measured electrode potential in such experiments reflects the  $iR$  drop through the oxide film and this may be several hundred volts. The diffusion layer in our experiments is analogous to these oxide films, and for this reason we are not surprised at the "abnormally" high electrode potentials encountered.

If, for example, reduction observed in the  $\text{AlCl}_3$  solutions were of solvent alone, there should be no potential break and no transition time, since the resistance between the working and reference electrodes would remain constant, there being no discharge and subsequent depletion of charged particles in the diffusion layer.

Any significance we had earlier attached to the magnitude of  $iT^{1/2}$  in  $\text{AlCl}_3$  solutions now seems specious. It is conceivable that but a fraction

of the total current is actually consumed by charged material. In this case the effective current to be used in calculating  $iT^{1/2}$  might be considerably less than the current actually applied. It is interesting to consider two possible extremes in behavior. For simplicity we assume the following equilibrium to predominate:  $2 \text{AlCl}_3 = \text{AlCl}_2^+ + \text{AlCl}_4^-$ . If all species are reduceable, and have equal mobilities then  $iT^{1/2}$  should be directly proportional to the total aluminum chloride concentration added. However, if all species are not reduceable and equilibrium is established relatively slowly with respect to the rate of discharge, then  $iT^{1/2}$  should not be constant with varying current at a given total aluminum chloride concentration, nor should it be proportional to the total aluminum chloride concentration. It is interesting to observe that there is a significant variation in  $iT^{1/2}$ , as seen in Figure 1 but we do not have enough good data to further interpret the system.

We are of the opinion that the aluminum species do play an important role in electrode behavior. An elucidation of the equilibria existing in this solution is desirable. The preceding discussion may indicate a possible technique for studying these equilibria in more detail.

To propylene carbonate solutions of  $\text{AlCl}_3$  were then added successive increments of  $\text{LiCl}$ . Well-defined chronopotentiograms were obtained with  $iT^{1/2}$  constant at constant  $\text{LiCl}$  concentration and directly proportional to the concentration of  $\text{LiCl}$  added. A gray to black film of lithium metal formed on the electrodes during cathodization.

The results of these chronopotentiometric investigations have been earlier reported and we considered them proof that the deposition of lithium was indeed well-behaved.

To expand our knowledge of these systems we have also studied the deposition of lithium from propylene carbonate solutions of  $\text{LiClO}_4$ . In Figure 2 are shown a series of chronopotentiograms obtained in 0.2 M  $\text{LiClO}_4$ . For comparison a chronopotentiogram obtained in the mixed  $\text{LiCl-AlCl}_3$  electrolyte is shown by the dashed line. It will be observed that the product  $iT^{1/2}$  increases with decreasing current. Such behavior is often observed and may be ascribed to the fact, alluded to earlier, that at lower currents the overvoltage for the second reduction may be lowered to such a degree that increasingly greater amounts of the total current are consumed in this reduction. The following data for  $iT^{1/2}$  as a function of concentration were obtained:

| Concentration of $\text{LiClO}_4$ | $iT^{1/2}$ (Average) in $\text{mA sec}^{1/2} \text{ cm}^{-2}$ |
|-----------------------------------|---|
| 0.1M                              | 18.4  |
| 0.2M                              | 34.3  |
| 0.3M                              | 56.0  |
| 0.5M                              | 93.0  |
| 1.0M                              | ----  |

The product,  $iT^{1/2}$  divided by the concentration, should be constant at all concentrations as is indeed observed. The experimental value of  $182 \text{ mA sec}^{1/2} \text{ cm mM}^{-1}$  is somewhat less than the value of 210 obtained in the



mixed  $\text{LiCl-AlCl}_3$  electrolytes and implied less mobility of ionic lithium in the perchlorate environment.

The physical, chemical, and electrochemical properties of lithium deposits in propylene carbonate. The physical appearance of the deposits is different depending on the conditions of deposition. In the  $\text{LiCl-AlCl}_3$  electrolytes the deposit varied from gray to black. At currents below about half the limiting current it was quite adherent, though mossy. At higher currents there was pronounced dendritic growth and significant amounts of deposit were sloughed off as the solutions were stirred. At currents close to and above the limiting current deposits were actually more adherent than at intermediate currents.

Deposits made from  $\text{LiClO}_4$  were generally more adherent than those made from  $\text{LiCl-AlCl}_3$  electrolytes. Silvery deposits were obtained at currents as low as  $2 \text{ mA cm}^{-2}$ . The deposits were progressively darker when formed at increasingly greater currents but remained adherent. Dendritic growth occurred primarily at the edges of the electrodes and was not nearly as serious as was the case with deposition from the chloride media.

Knowing that the deposition behavior of lithium was well-behaved we anticipated no difficulty in successfully and completely re-oxidizing the deposits anodically. This was not possible, however. In the Second Quarterly Report extensive discussion was presented of the behavior observed. The work of other groups has since confirmed our observations. Anodic efficiency decreases

with increasing deposition current, and with increasing amount of deposit. Further investigations have simply confirmed our earlier observation. Anodic efficiencies for deposits made from  $\text{LiClO}_4$  solutions were even lower than in chloride media. This observation was important since it had been suggested that the reason for failure to obtain good anodic efficiency lay in the fact that occlusion of aluminum species in the deposit might occur. Since there are no aluminum species present in the  $\text{LiClO}_4$  solutions and anodic efficiencies nevertheless remained low this explanation appears not to have general validity.

We further emphasize the fact that anodic efficiencies were not critically dependent on the current of anodization, and that efficiencies could not be increased by anodically discharging the deposits intermittently rather than continuously. Therefore we are of the opinion that the failure to obtain good anodic efficiency lies in the conditions of deposition rather than of redissolution. The effect of possible passivation on anodization seems to be discounted.

Chemical analysis of the deposits was continued following the procedure discussed in the Second Quarterly Report. This is a titrimetric method in which the amount of lithium deposited is determined by titrating the amount of base released on reaction of lithium with aqueous solution. In previous analyses it was necessary to rinse the electrode with propylene carbonate to remove excess electrolyte containing +3 aluminum species. When depositions are made from  $\text{LiClO}_4$  solution this rinsing is not necessary, the electrode

can be immersed directly in water and the released base titrated. When such depositions were made from  $\text{LiClO}_4$  solutions, 100% current efficiency was obtained, indicated by the fact the equivalents of hydroxide released on reaction with water was exactly equal to the equivalents of current passed on deposition within the experimental error of a few percent.

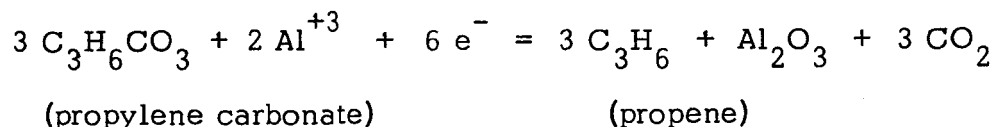
In our analysis of deposits made from  $\text{LiCl-AlCl}_3$  solution we had never studied deposits made at currents several times larger than the limiting current, and the deposits had always been rinsed, which resulted in mechanical removal of some of the deposit. During this quarter further studies were done in which depositions were made from  $\text{LiCl-AlCl}_3$  solutions and the deposit was reacted directly with excess standard acid to prevent hydrolysis of +3 aluminum species. The results were quite surprising as shown below in which cathodization from propylene carbonate, 0.105 M in  $\text{AlCl}_3$ , 0.072 M in  $\text{LiCl}$ . Cathodizations performed on  $1.2 \text{ cm}^2$  polished copper for a total of 12,500 millicoulombs  $\text{cm}^{-2}$ . Calculated limiting current for lithium in this solution is  $7.2 \text{ mA cm}^{-2}$ .

| <u>Current (<math>\text{mA cm}^{-2}</math>)</u> | <u>Current efficiency</u> |
|---|---------------------------|
| 8.6   | 45%                       |
| 17.2  | 67%                       |
| 25.8  | 70%                       |
| 36.5  | 90%                       |
| 47.0  | 90%                       |

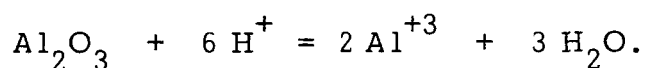
At a current of  $47 \text{ mA cm}^{-2}$ , which is 6.5 times the limiting current, the current efficiency for lithium deposition should only be about 15%.

Clearly, our procedure for analyzing the deposits is quite imperfect

if deposition does not proceed as cleanly as was assumed. For example, a reaction of the following type may occur at currents above the limiting current for lithium.



When the deposit is reacted with excess standard acid:



The equivalence between current passed and base produced is preserved. However, it will be recalled that, in the absence of LiCl, no deposit is produced on prolonged electrolysis.

Since the cause of incomplete anodization of electrodeposited lithium lies in the deposition step itself, it is important to consider other processes occurring on cathodization. It may be expected that a small amount of co-deposition of other material (such as  $\text{Al}_2\text{O}_3$ ) may seriously inhibit successful re-anodization.

It seems reasonable to expect that there may be fundamental differences between deposition made from aqueous solutions and those made from organic solvents such as propylene carbonate. These differences may be most strongly evidenced in the kinetics of charge transfer across the electrode/electrolyte interface and the kinetics of crystallization. The cause for these differences may lie primarily in the great difference in size between the water molecule and the organic solvent molecule. As a result of such

fundamental differences it seems not unreasonable to suppose that a deposit of lithium made from propylene carbonate may more closely approximate a fine metal powder dispersed through a "glue" of co-deposited oxide. Inefficient anodization of such a material would be expected.

Further experiments in this extremely important area will await better knowledge of the composition of the electrolyte itself. Without this knowledge it is quite impossible to develop a satisfactorily comprehensive model for the lithium electrode.

### PART III. IMPURITIES IN PROPYLENE CARBONATE

A question of major concern is whether or not there may exist in propylene carbonate deleterious impurities. How may these impurities be detected? How may they be eliminated? We are immediately concerned only with those impurities which directly or indirectly affect electrode behavior.

In previously reported work, we had suggested that impurities are introduced into the solution through solvent decomposition, occurring primarily as a result of the excessive heat of solution evolved when anhydrous  $\text{AlCl}_3$  is added directly to propylene carbonate. The presence of this impurity is evidenced in three ways: the deep golden-brown color of the solution, the fairly rapid chemical stripping of electrodeposited lithium, and the presence of a polarographic limiting current at potentials below that required for lithium reduction. Prolonged electrolysis at constant potential removes most of the impurity.

Propylene carbonate solutions of  $\text{AlCl}_3$  of better quality have been prepared by reacting 99.999% pure aluminum wire in diethyl ether with anhydrous hydrogen chloride. On completion of reaction the aluminum trichloride etherate was refluxed to remove excess hydrogen chloride. Propylene carbonate was added through a dropping funnel, displacing the complexed ether. The mixture was then heated under vacuum to remove the diethyl ether. The resulting solution was then transferred to a volumetric flask and brought to volume with propylene carbonate. The resultant solution is only pale yellow

and exhibits properties similar to those of electrolytically purified solutions. Solutions prepared using 99.3% aluminum were not satisfactory. Excessively high temperature during the removal of ether by distillation also results in unsatisfactory solutions.

We were not satisfied that the above procedures eliminated impurities to a satisfactory extent. The electrometric measurements by which the presence and removal of impurities is detected were discordant, and we became less confident that polarographic measurements are an accurate reflection of the amount of impurity present. Polarographic measurements are made by holding the working electrode potential constant in stirred solution and measuring the resultant steady state current. Distressing was the fact that as much as twenty minutes were sometimes required before a satisfactorily constant steady state current was reached. Before this point the current steadily though slowly decreased. In earlier work we had not waited long enough for a steady state current to be reached, being deluded by the fact that for periods of a few minutes the current does indeed appear to be relatively constant.

We have concluded that, during reduction of the impurity, the electrode becomes in some way de-activated for further reduction. The behavior is as if the electrode becomes coated with some inhibiting material, thus reducing the effective area remaining, and reducing the limiting current. As a result the steady state current measured is an inaccurate reflection of impurity concentration. By the same token a series of chronopotentiograms performed on the same electrode without intermediate cleaning show steadily

decreasing values of  $iT^{1/2}$ . When chronopotentiograms are made at different currents, each on a freshly polished electrode, more concordant results are obtained. In Figure 3 are shown a series of chronopotentiograms obtained in an electrolytically purified solution. For some appreciation of the significance of the value for  $iT^{1/2}$  of  $3 \text{ mA sec}^{1/2} \text{ cm}^{-2}$  let us suppose that this corresponds to the reduction of water. If the mass transfer parameters of water in propylene carbonate are the same as those of lithium this value for  $iT^{1/2}$  would correspond to a water concentration of only about 0.015 M (less than 0.03% by weight).

As discussed in previous reports the relationship between  $iT^{1/2}$  and the limiting current is such that the limiting current is about half the value of  $iT^{1/2}$ . Thus we would predict a limiting current for impurity reduction in this solution of about  $1.5 \text{ mA cm}^{-2}$ . The actual value measured polarographically was less than  $0.5 \text{ mA cm}^{-2}$ , clear indication of surface deactivation.

A third type of experiment which is instructive is to measure the current during extended pre-electrolysis. For pre-electrolysis copper coils, about  $100 \text{ cm}^2$ , were used as working electrodes. The potential of the electrode was held at about -2.5 V versus the silver reference electrode and the current recorded. Theory predicts that the current should decay according to the equation:

$$i = a e^{-bt}$$

From a plot of the logarithm of current versus time one can determine the two constants,  $a$  and  $b$ . Integration of the equation  $dQ = i dt$  enables one to



determine the total coulombs of active material reduceable at this potential.

A typical experiment is depicted in Figure 4. From this plot one calculates values for  $a$  and  $b$  in the preceding equation of 33 mA and  $1.2 \times 10^{-4} \text{ sec}^{-1}$ . Integration of the differential equation from zero to infinite time gives a total of  $3 \times 10^5$  millicoulombs of electroreduceable impurity in the 200 ml. of solution electrolyzed, corresponding to a concentration of 0.015N. This would correspond to a chronopotentiometric  $iT^{1/2}$  before electrolysis of about  $3 \text{ mA sec}^{1/2} \text{ cm}^{-2}$ , and a limiting current of about  $1.5 \text{ mA cm}^{-2}$ . This is reasonably close to the actual magnitude of these quantities prior to electrolysis, but more refined experiments should be performed. Background impurities can never be completely eliminated by electrolysis. This suggests that part of the supposed "impurity" is some species in equilibrium with other constituents in the solution and which is continuously regenerated by this equilibrium as electrolytic removal progresses.

The importance of having more detailed knowledge regarding background impurities becomes more clear when one considers the significant role small amounts of additives play in ordinary aqueous solution electrodeposition. The futility of attempting to obtain reliable electrochemical data in systems for which no consideration of the presence of impurities is given, other than in the careful preparation of reagents, is obvious. Data so obtained is of questionable significance.

We now address ourselves to the question of the role water plays as an impurity in propylene carbonate solutions. That water may be deleterious

is obvious; the actual role it may play is less obvious. We are currently engaged in studies concerning the actual behavior observed as a result of the deliberate addition of water.

One would suspect that, on the addition of water, hydrolysis should occur thus:

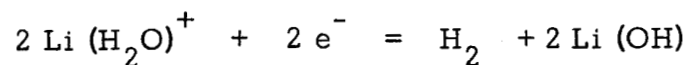


It is not so important what the actual products are as is the question of their nature. One of the products should be an insoluble basic aluminum salt, the other should be a material containing active hydrogen -- hydrogen in a form more easily reduceable than lithium.

The presence of material containing active hydrogen should be readily apparent from chronopotentiometric measurements. Pre-purified solutions were examined chronopotentiometrically and the chronopotentiograms obtained were similar to those shown in Figure 3. The product,  $iT^{1/2}$ , should increase proportionately as water is added, if material containing active hydrogen is formed. This was not found to be true. To a solution initially 0.105 M in  $\text{AlCl}_3$  and 0.072 M in  $\text{LiCl}$  was added, incrementally, water to a final total concentration of 0.6 M. The increase in  $iT^{1/2}$  was only about  $3 \text{ mA sec}^{1/2} \text{ cm}^{-2}$ . The increase expected would be of the order of  $200 \text{ mA sec}^{1/2} \text{ cm}^{-2}$ . The water has not produced material containing active hydrogen.

We are currently investigating the effect of water on lithium deposition and on the anodization of silver and copper. Our results are as yet

inconclusive but there is some evidence that, on cathodization, processes such as the following may occur, producing insulating oxide films:

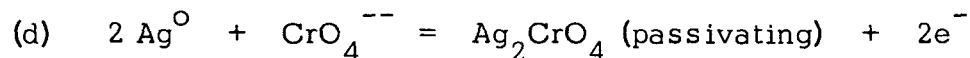
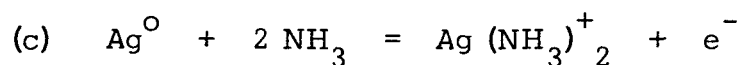
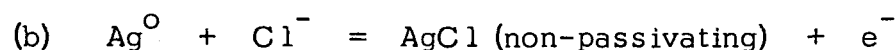
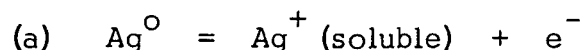


In these experiments we are also analyzing any gas evolved on the addition of water and the precipitate produced, as well as measuring the conductivity. Our results, though incomplete, cannot be explained on the basis of any simple hydrolysis reaction.

#### PART IV. ANODIC BEHAVIOR OF METALS IN PROPYLENE CARBONATE

During this quarter we have begun more intensive investigations into the anodic behavior of various metals in propylene carbonate electrolytes. We have studied the anodic oxidation and subsequent cathodic reduction on aluminum, iron, cobalt, nickel, copper and silver. As with our examination of lithium electrodes we are not only interested in the electrode behavior per se, but also in the degree to which such behavior reflects the electrolyte composition.

In aqueous solution we consider the following systems:



In reaction (a) there will be no anodic transition time. If the current is immediately reversed after some period of time the larger fraction of soluble silver ions will have diffused sufficiently far away from the electrode to be unavailable for subsequent re-reduction. Theory predicts that 1/3 of the silver ions produced on anodization will be available for reduction when the current is reversed. This number, 1/3, is general for all systems in which the electrolysis product is soluble. There will exist a cathodic transition time when this reduction is complete, equal to 1/3 the anodization time.

In reaction (b) there will be an anodic transition time related to the

concentration of chloride ions in the electrolyte. When the current is reversed all of the silver chloride will be available for subsequent reduction and the cathodic transition time will be equal to the time previous anodization was continued.

In reaction (c) there will be an anodic transition time related to the concentration of ammonia. Subsequent cathodic transition times will be equal to  $1/3$  the preceding time of anodization.

In reaction (d) there will be an anodic transition time, but this will not be directly related to the concentration of chromate in solution since the film itself inhibits ionic movement. Transition times will be significantly less than those calculated from mass transfer parameters. Subsequent cathodization ideally should result in complete re-deposition of silver.

The preceding discussion indicates how constant current anodization followed by current reversal may be expected to yield useful information about the behavior of the electrodes in various media.

In our experiments in propylene carbonate the most reproduceable and clear-cut behavior was observed with silver electrodes. In Figure 5 are shown the results obtained when a polished silver electrode is subjected to anodic-cathodic cycling in propylene carbonate solutions of  $\text{LiClO}_4$ . The cathodic transition times are satisfactorily close to  $1/3$  of the previous anodization time to indicate that the product of electrolysis is a soluble silver ion species. This process is observed to occur over a wide range of currents. The variation in potential for the different currents is the large  $iR$  drop. The magnitude of

the effective resistance resulting in this iR drop can be calculated from the relationship between current and potential. A value of about 100 ohms is obtained.

Identical behavior is observed for copper electrodes in propylene carbonate solutions of  $\text{LiClO}_4$ . Typical results are shown in Figure 6.

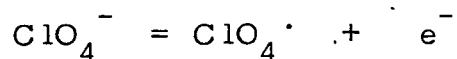
The reverse cathodization with both silver and copper electrodes produces a black film of finely divided metal. The properties of such a surface differ from those of mirror-bright surfaces; therefore one must normally exercise extreme caution in the interpretation of data based on repeated oxidation-reduction cycling on the same electrode. Although the chronopotentiograms shown in Figures 5 and 6 were separately obtained on freshly polished electrodes it was found that no significant variations in potential or cathodic transition time were observed if measurements were made repeatedly on the same electrode.

If anodization of copper and silver is continued without subsequent current reversal, the surfaces of the electrodes become etched as metal is anodically dissolved into the solution.

The behavior of iron, cobalt, and nickel electrodes in  $\text{LiClO}_4$  solutions is radically different from that of copper and silver. In Figure 7 are shown anodic chronopotentiograms obtained on polished cobalt electrodes in 1 M  $\text{LiClO}_4$ . Repeated anodizations on the same electrode do not produce significant changes in the chronopotentiograms, indicating that the products of anodization do not noticeably change the properties of the surface.

There is very little surface etching, and it appears that cobalt itself is not anodized to the metal ion.

Originally we suspected the anodic reaction to be:



from the magnitude of  $iT^{1/2}$ . If the reaction involves but one electron and if the mass transfer parameters of the perchlorate ion are equal to those of lithium, then one would calculate a value for  $iT^{1/2}$  in 1 M lithium perchlorate of  $180 \text{ mA sec}^{1/2} \text{ cm}^{-2}$ , which is reasonably close to the experimentally observed value. This is not the case, however. It was found that  $iT^{1/2}$  actually increased for more dilute solutions of lithium perchlorate.

The nickel and iron electrodes behave identically to the cobalt electrode and the product,  $iT^{1/2}$ , is the same as on cobalt. It is usually necessary to perform several preliminary anodizations on nickel and iron before satisfactorily reproducible results are obtained. Evidently there exists some surface film on nickel and iron which must be destroyed before reproducibility is achieved. This is not surprising and is a problem often encountered in making chronopotentiometric measurements.

As yet we have no explanation for the mysterious anodic behavior displayed by iron, cobalt, and nickel in  $\text{LiClO}_4$  solution.

To the solutions of  $\text{LiClO}_4$  were added incrementally small amounts of  $\text{AlCl}_3$ . The behavior of the silver electrode in such media is typified by the curves shown in Figure 8. It is clear that an insoluble chloride is

produced on anodization since between 60 and 80% recovery is obtained on subsequent cathodization. Actually the recovery is normally greater than 95% and the reason the curves shown in Figure 8 fail to show this is as follows: It is characteristically observed that it is difficult to reduce the last traces of any salt film formed on a metal, just as it is often difficult to anodically dissolve the last traces of a metal film. The total amount of film formed during the electrolyses shown in Figure 8 is quite small and the effect described above would be expected to substantially diminish the succeeding cathodic efficiency. When anodizations are continued over long periods of time the recovery of anodic salt increases proportionately to nearly 100%.

The behavior of the copper electrodes in the  $\text{LiClO}_4\text{-AlCl}_3$  solutions is similar to that of silver. However, subsequent reduction is more complicated. In Figure 9 are shown the results of a series of cathodizations, all performed at  $4.25 \text{ mA cm}^{-2}$  following anodization at the same current. The only difference between each electrolysis was that the times of anodization were varied. We have not yet felt it instructive to attempt to develop any explanation for this complicated cathodic behavior.

A second major difference between the copper and silver electrodes lies in the stability of the deposit formed during anodization. The silver chloride film is quite stable, and a negligible amount is lost after stirring for an hour. The copper deposit is not stable and is lost (probably by re-dissolution) after ten minutes.

Anodic chronopotentiograms were done on silver electrodes at various



currents to determine if there was any relationship between the concentration of  $\text{AlCl}_3$  and  $iT^{1/2}$ . The results of a typical investigation are shown in Figure 10. It is instructive to consider the significance of the value for  $iT^{1/2}$  of  $11.7 \text{ mA sec}^{1/2} \text{ cm}^{-2}$ , since it was found that  $iT^{1/2}$  is indeed proportional to the concentration of  $\text{AlCl}_3$ . The value of  $iT^{1/2}$  for lithium reduction from a  $0.025 \text{ M}$  solution of  $\text{LiClO}_4$  is only  $4.5 \text{ mA sec}^{1/2} \text{ cm}^{-2}$ . If the mass transfer parameters of  $\text{AlCl}_3$  are equal to those for lithium, and if only one chloride is lost from  $\text{AlCl}_3$  for silver chloride deposition  $iT^{1/2}$  should also be 4.5. The fact that it is nearly three times larger strongly suggests that more than one chloride may be lost per aluminum ion. This is quite significant when one considers what must happen to the "naked" aluminum ion left at the electrode after being stripped of its chloride ions. We suspect that these aluminum ions strongly catalyze a rapid and localized decomposition of solvent at the electrode surface. Further evidence of this is given in the next paragraph.

If, in a solution of  $\text{LiClO}_4$  and  $\text{AlCl}_3$ , silver is cathodized at a moderate current (e.g.  $5 \text{ mA cm}^{-2}$ ), the potential immediately rises to about  $-3 \text{ V}$  and lithium deposition occurs. If, however, the silver is anodized at  $5 \text{ mA cm}^{-2}$  and the current reversed rather anomalous behavior is observed. First all of the silver chloride is reduced, with essentially 100% efficiency. However, after the reduction of the silver chloride the potential does not immediately jump to  $-3 \text{ V}$  as would be expected. Instead there is a very slow rise in potential, which, while not very reproduceable, seems to indicate that, during anodization, there has formed at the electrode surface some impurity

which itself is capable of reduction. We suspect the process occurring is that described in the preceding paragraph. We further suspect that the impurity formed at the electrode surface might be identical with that formed when aluminum trichloride is added directly to propylene carbonate.

Returning to the behavior of electrodes in  $\text{LiClO}_4\text{-AlCl}_3$  solutions we consider cobalt, nickel, and iron electrodes. The addition of aluminum chloride produces some change in the chronopotentiograms, and  $iT^{1/2}$  decreases slightly. It appears that there may be some formation of passivating chloride films on the three metals but the requisite data is not yet complete. It is certainly true that any reduction of anodization products proceeds with very large overvoltage, suggesting that any couples involving metallic iron, cobalt, or nickel may never prove useful for secondary battery cathodes.

Reference has not yet been made to the behavior of aluminum electrodes. Anodic transition times are obtained but we have had no success whatsoever in obtaining any degree of reproducibility and can make no meaningful statements regarding the aluminum electrode.

We are certain that the anodic behavior of these metals in various electrolytes will provide more direct insight into the electrolyte properties and are actively engaged in examining such behavior with other systems.

## PART V. OTHER INVESTIGATIONS

A number of other systems have been examined during the course of our work. Since most of this work is in an exploratory stage we defer detailed discussion until a later date. We have been investigating the deposition and subsequent reanodization of aluminum from a solution of ethyl pyridinium bromide and  $\text{AlCl}_3$  in toluene, of beryllium from a solution of diethyl beryllium and  $\text{BeCl}_2$  in tetrahydrofuran, and of potassium from propylene carbonate solutions of potassium hexafluorophosphate. Both aluminum and beryllium can be satisfactorily deposited from the solutions indicated, and reanodization is, in some cases, more efficient than for the reanodization of lithium. Potassium can be deposited with 100% current efficiency but anodization efficiency is extremely poor.

We have also begun further investigations in acetonitrile and butyrolactone solutions. The results to date indicate the existence of the same kind of problems found with propylene carbonate but to an even more severe extent.

It was earlier reported that a noticeable improvement in the behavior of the copper electrode on anodic-cathodic cycling was noted in solutions of  $\text{AlCl}_3$  and  $\text{KPF}_6$ . We have not found any significant improvement in solutions of  $\text{KPF}_6$  which do not also contain  $\text{AlCl}_3$ . However, our interest in the use of fluoride species remains quite active.

## APPENDIX. EXPERIMENTAL PROCEDURES

We have continued to use the procedures described in the Second Quarterly Report and preceding reports. A standard H-cell is used for the electro-metric measurements in which a glass frit separates the working and auxiliary electrode chambers. A platinum coil serves as the working electrode, and the working and reference electrodes are contained together in a "lollipop" type electrode described in the Second Quarterly Report. We note that the use of this type electrode, embodying six working electrodes, has greatly increased the amount of data we can obtain, since for many investigations it is necessary to pre-treat the electrode in some way after each run. The use of such an electrode decreases the time and effort required for necessary pre-treatment six-fold.

Commercially available, electrically controlled constant current supplies and potentiostats are used, the characteristics of which are well known. Strip-chart potentiometric recorders are used for following potential and current variations. Mercury relays are extensively used in switching.

We consider briefly the electrometric techniques employed in our work.

Chronopotentiometry. Chronopotentiograms (or charging curves) are obtained when an electrode, in quiescent solution, is perturbed by the application of a constant current. The resultant potential of the working electrode is measured versus an appropriate reference electrode, and the variation of potential with time constitutes a chronopotentiogram. The situation is exactly analogous to that prevailing when a battery is cycled through charge

and discharge and the voltage recorded with the difference that in chronopotentiometry the potential of but one electrode is measured so that the effect of the perturbation is unambiguously assignable to one electrode.

Potentiostatic measurements. In such measurements the potential of the working electrode is held constant. The ability to do this demands a degree of instrumental sophistication not necessary with constant current measurements. In essence a potentiostat comprises two instruments. One instrument acts as an electrometer, sensing the potential of the working electrode versus the reference electrode. In order that this potential should remain constant the current supplied to the working electrode must be appropriately varied. The potentiostat effectively incorporates a second instrument which controls the current automatically to maintain the desired potential. It must be emphasized that the potentiostatic measurements performed in our experiments differ in principle from measurements made by simply applying a constant voltage across two electrodes.

Polarography is a type of potentiostatic measurement in which a steady state condition of solution agitation prevails. This may involve mechanical stirring, or agitation by convection. The resultant steady state current is measured, and a plot of steady state current versus potential constitutes a polarogram. We stress the fact that polarography does not imply the use of a dropping mercury electrode.

Potentiostatic measurements may also be made in quiescent solution and the initial current decay recorded.

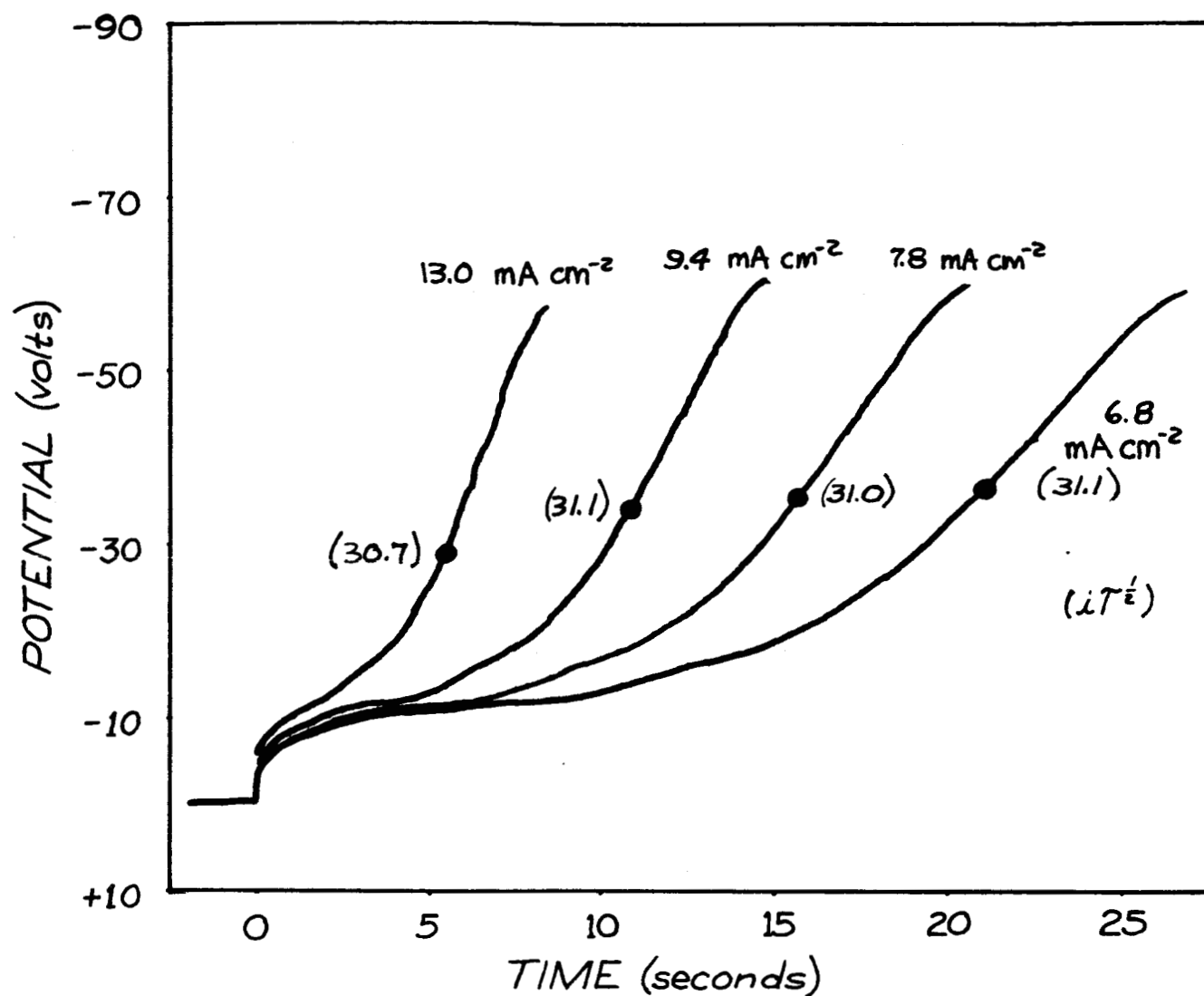


Figure 1 Constant current cathodic charging curves obtained on polished cobalt electrode in propylene carbonate, 0.35 M in  $\text{AlCl}_3$ . Figures in parentheses are  $iT^{1/2}$  in  $\text{mA sec}^{1/2} \text{cm}^{-2}$ , calculated from transition times indicated by black circles on the charging curves.

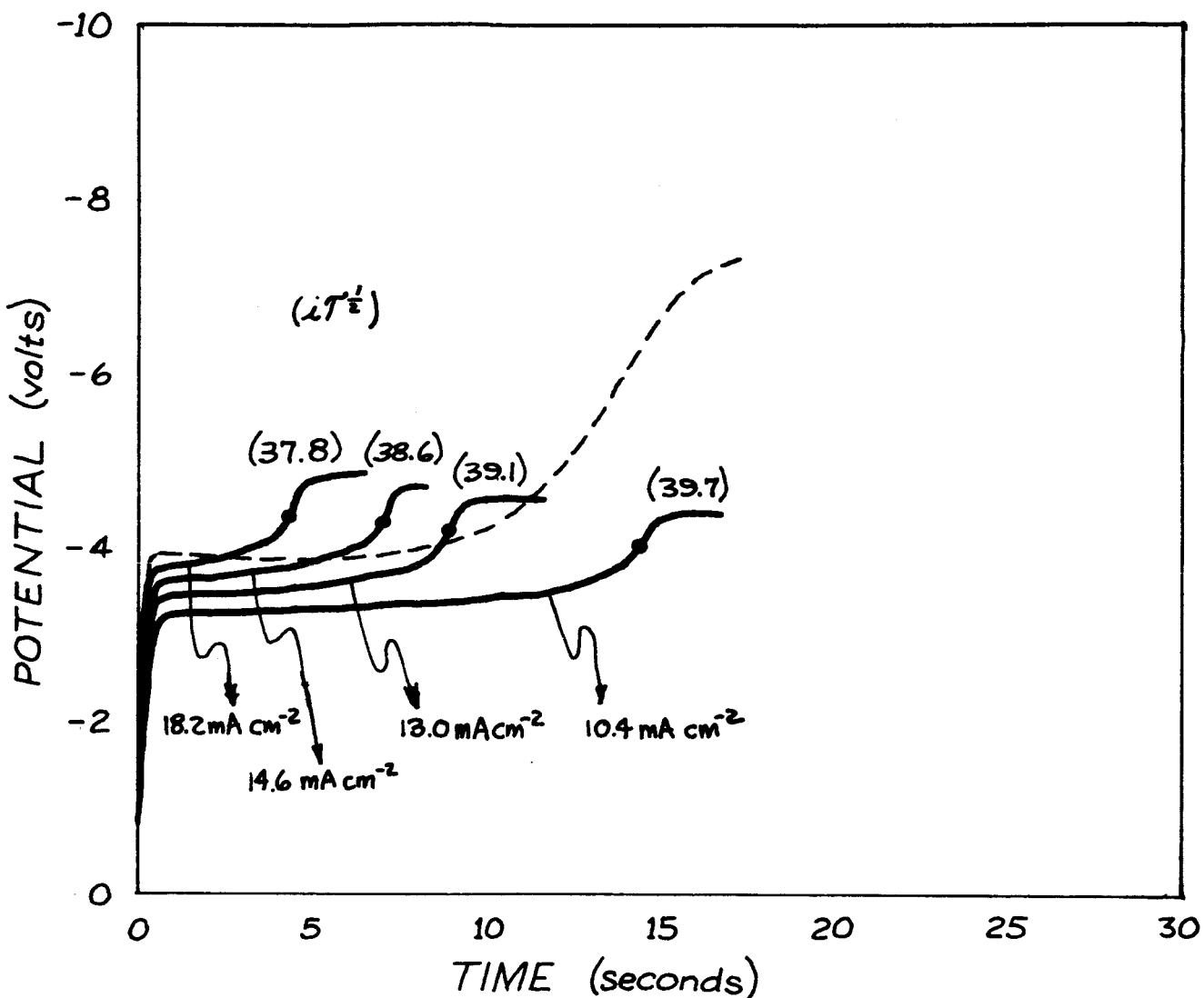


Figure 2 Constant current cathodic charging curves obtained on polished cobalt electrodes. Solid line charging curves represent cathodization in propylene carbonate, 0.2 M in  $\text{LiClO}_4$ . Figures in parentheses are  $i\tau^{1/2}$  in  $\text{mA cm}^{-2} \text{sec}^{1/2}$ , calculated from transition times indicated by black circles on the charging curves. The dotted line charging curve, shown for comparison, represents cathodization in propylene carbonate, 0.5 M in  $\text{AlCl}_3$  and 0.14 M in  $\text{LiCl}$ . In all cases reduction, prior to the potential rise, is that of +1 lithium to the metal.

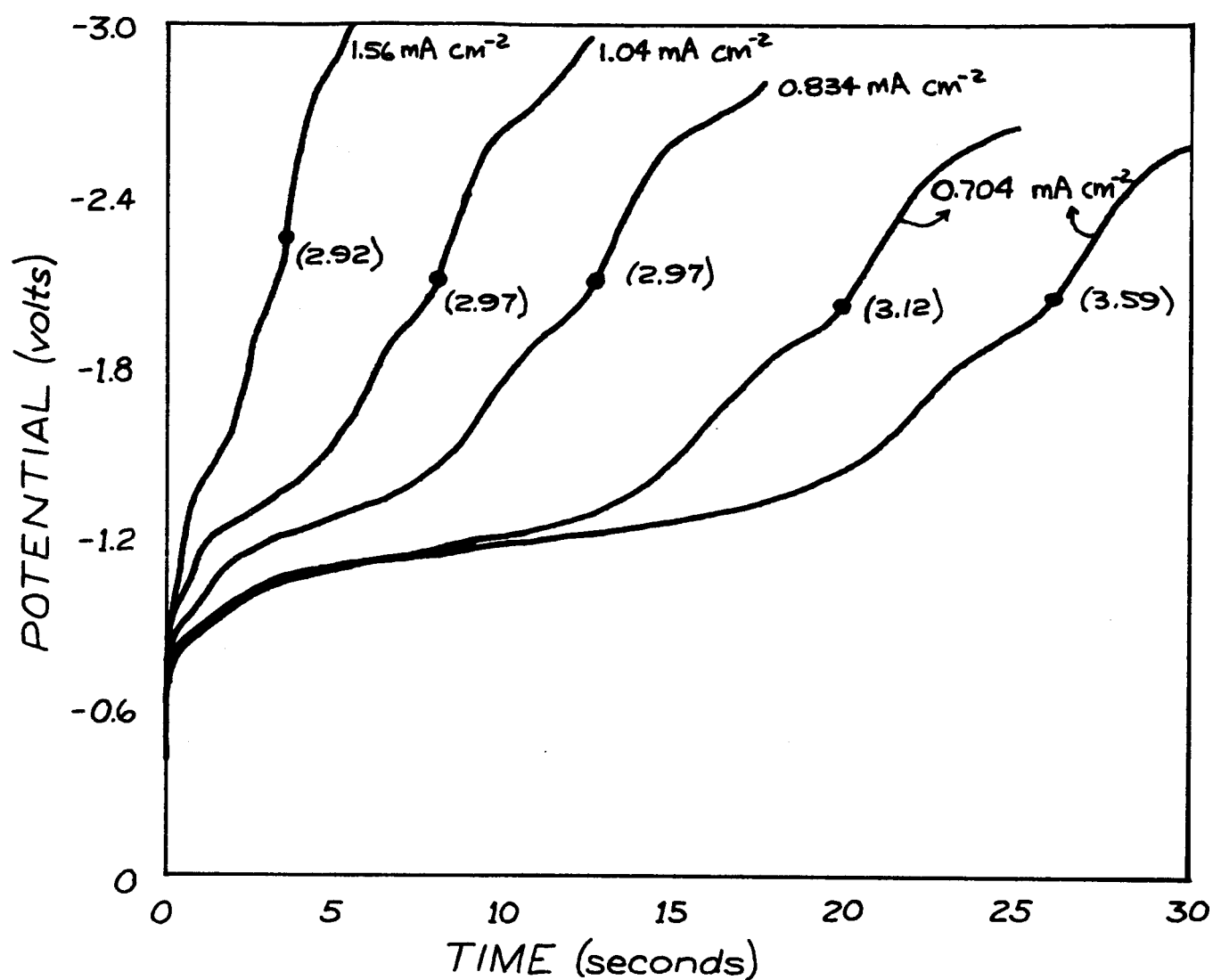


Figure 3 Constant current cathodic charging curves obtained on polished copper electrodes in propylene carbonate, 0.104 M in  $\text{AlCl}_3$  and 0.072 M in  $\text{LiCl}$ . The products,  $iT^{1/2}$  in  $\text{mA cm}^{-2} \text{sec}^{1/2}$ , given in parentheses, are calculated using the transition times indicated by the solid circles. The reduction, discussed in the text, is that of impurities present in the solution.



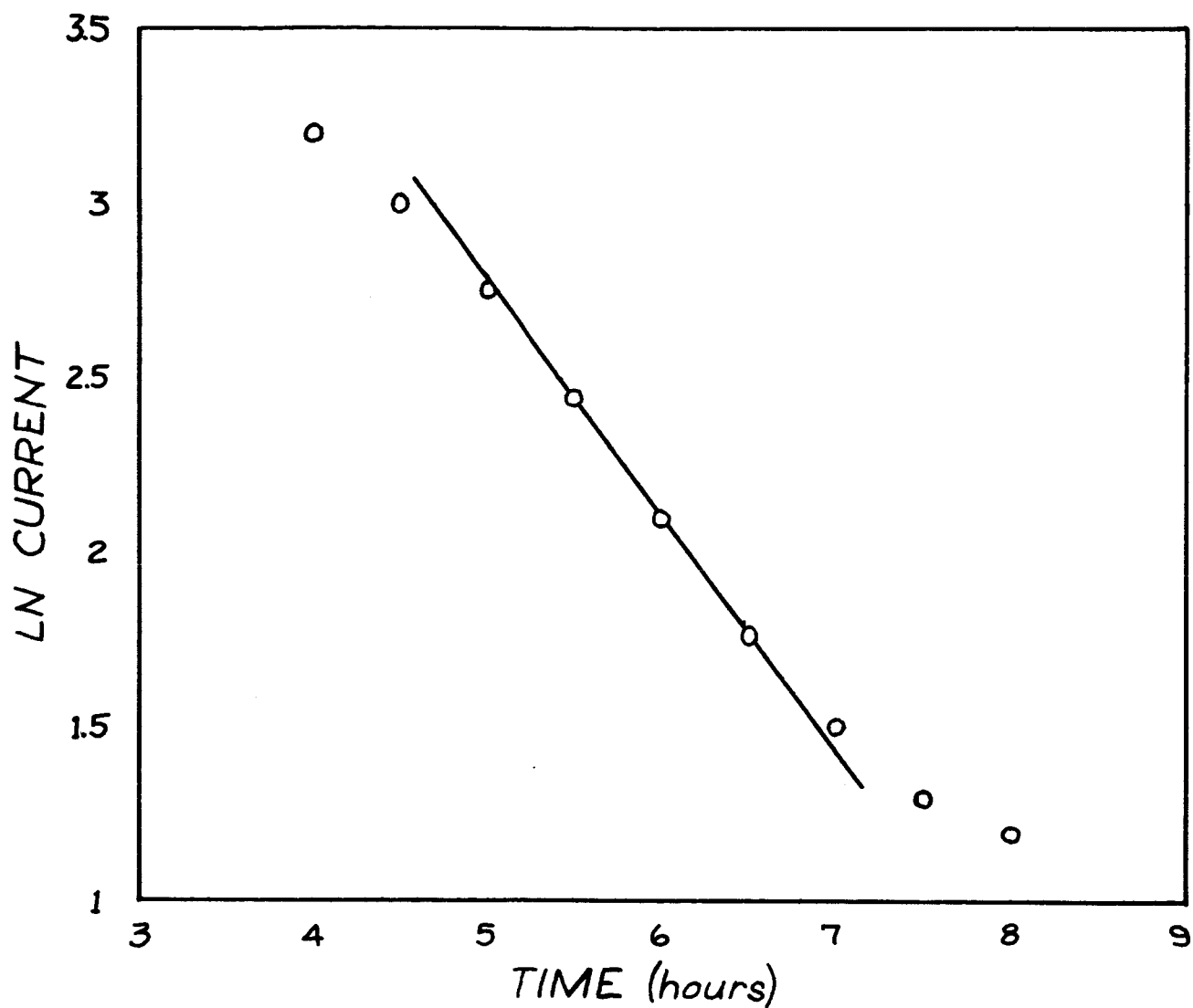


Figure 4 Decay of electrolysis current with time, showing removal of electroactive impurities. Electrolysis conducted potentiostatically at  $-2.5$  V versus silver reference electrode on  $100\text{ cm}^2$  copper coil in propylene carbonate,  $0.225\text{ M}$  in  $\text{AlCl}_3$  and  $0.2\text{ M}$  in  $\text{LiCl}$ . (Logarithm of current to the base  $e$ .)

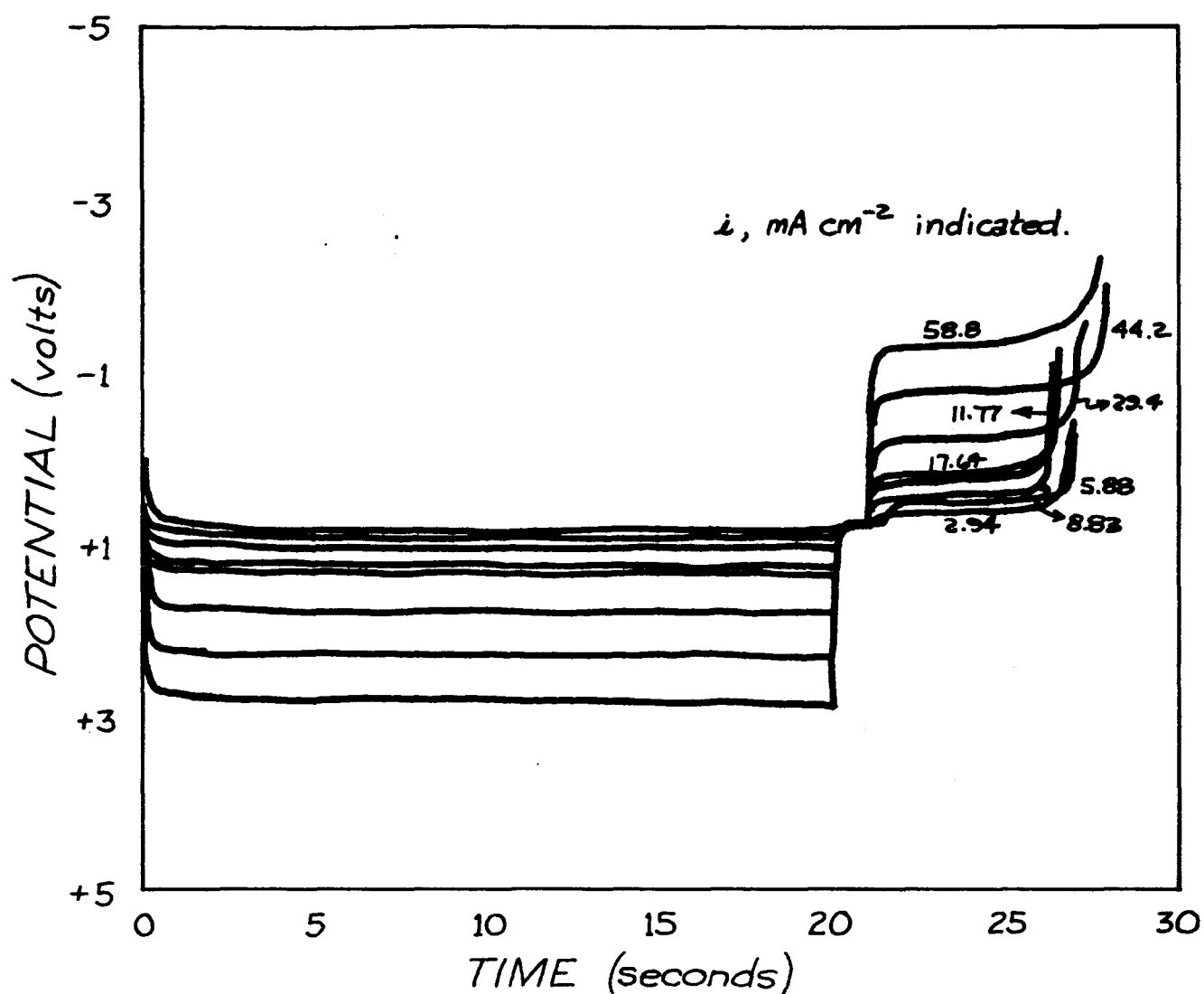


Figure 5 Constant current anodic-cathodic charging curves obtained on polished silver electrodes in propylene carbonate, 1 M in  $\text{LiClO}_4$ . Cycling program consisted of anodization at current indicated for 20 seconds, 1 second pause, and cathodization at the same current as the previous anodization. Electrode reactions are the anodic oxidation of silver to a soluble ionic species, followed by reduction of this species to metallic silver.

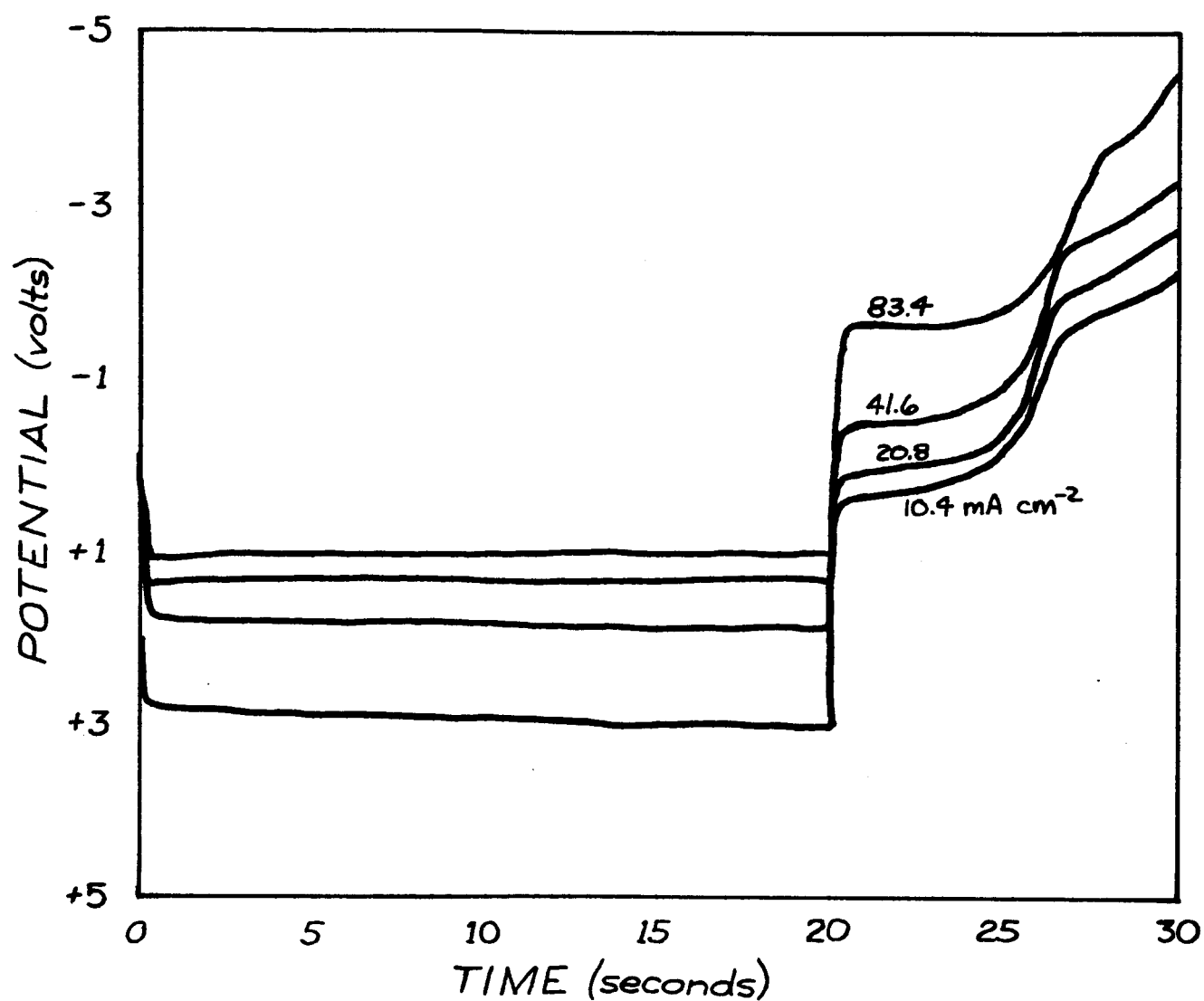


Figure 6 Constant current anodic-cathodic charging curves obtained on polished copper electrodes in propylene carbonate, 1 M in  $\text{LiClO}_4$ . Cycling program consisted of anodization at current indicated for 20 seconds, followed by immediate cathodization at the same current as the previous anodization. Electrode reactions are the anodic oxidation of copper to a soluble ionic species, followed by reduction of this species to metallic copper.

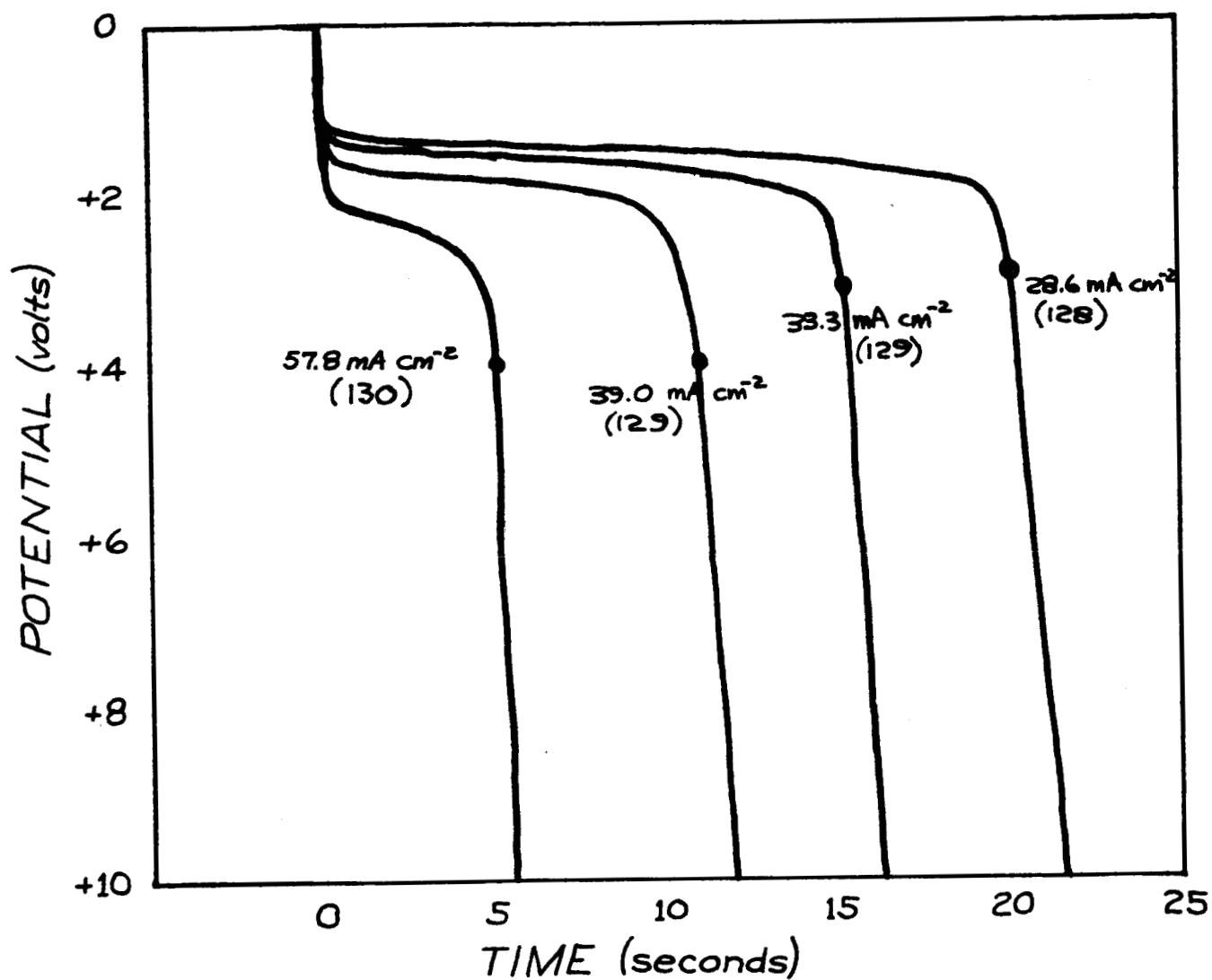


Figure 7 Constant current anodic charging curves obtained on polished cobalt electrodes in propylene carbonate, 1 M in  $\text{LiClO}_4$ . The products,  $iT^{1/2}$  in  $\text{mA cm}^{-2} \text{ sec}^{1/2}$  given in parentheses, are calculated using the transition times indicated by the solid circles. The oxidation, discussed in the text, appears not to be that of cobalt metal.

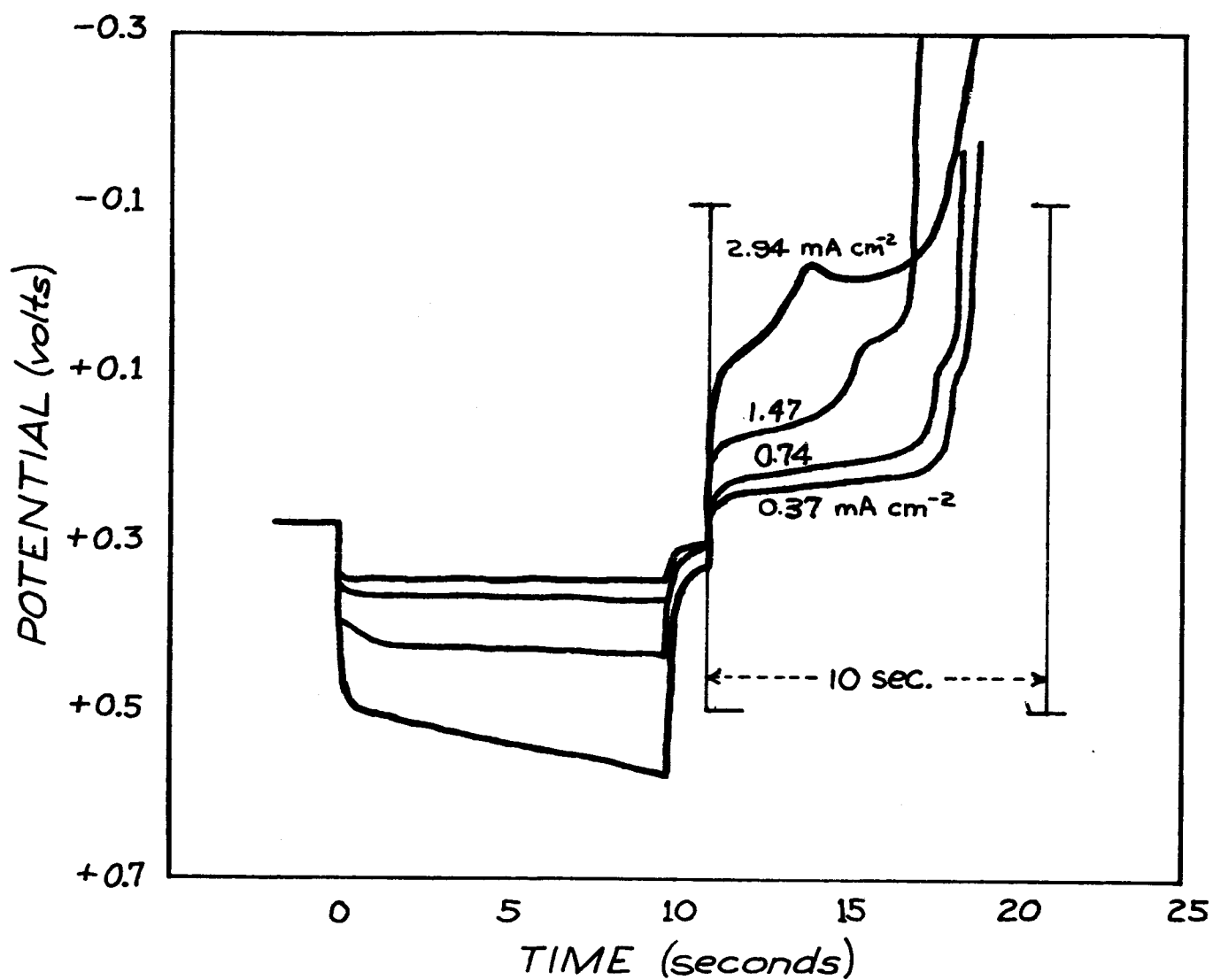


Figure 8 Constant current anodic- cathodic charging curves obtained on polished silver electrodes in propylene carbonate, 1 M in  $\text{LiCl}_4$ , and 0.1 M in  $\text{AlCl}_3$ . Cycling program consisted of anodization at current indicated for 20 seconds, 1 second pause, and cathodization at the same current as the previous anodization. Electrode reactions are the anodic oxidation of silver to an insoluble chloride salt, followed by reduction of this salt to metallic silver.

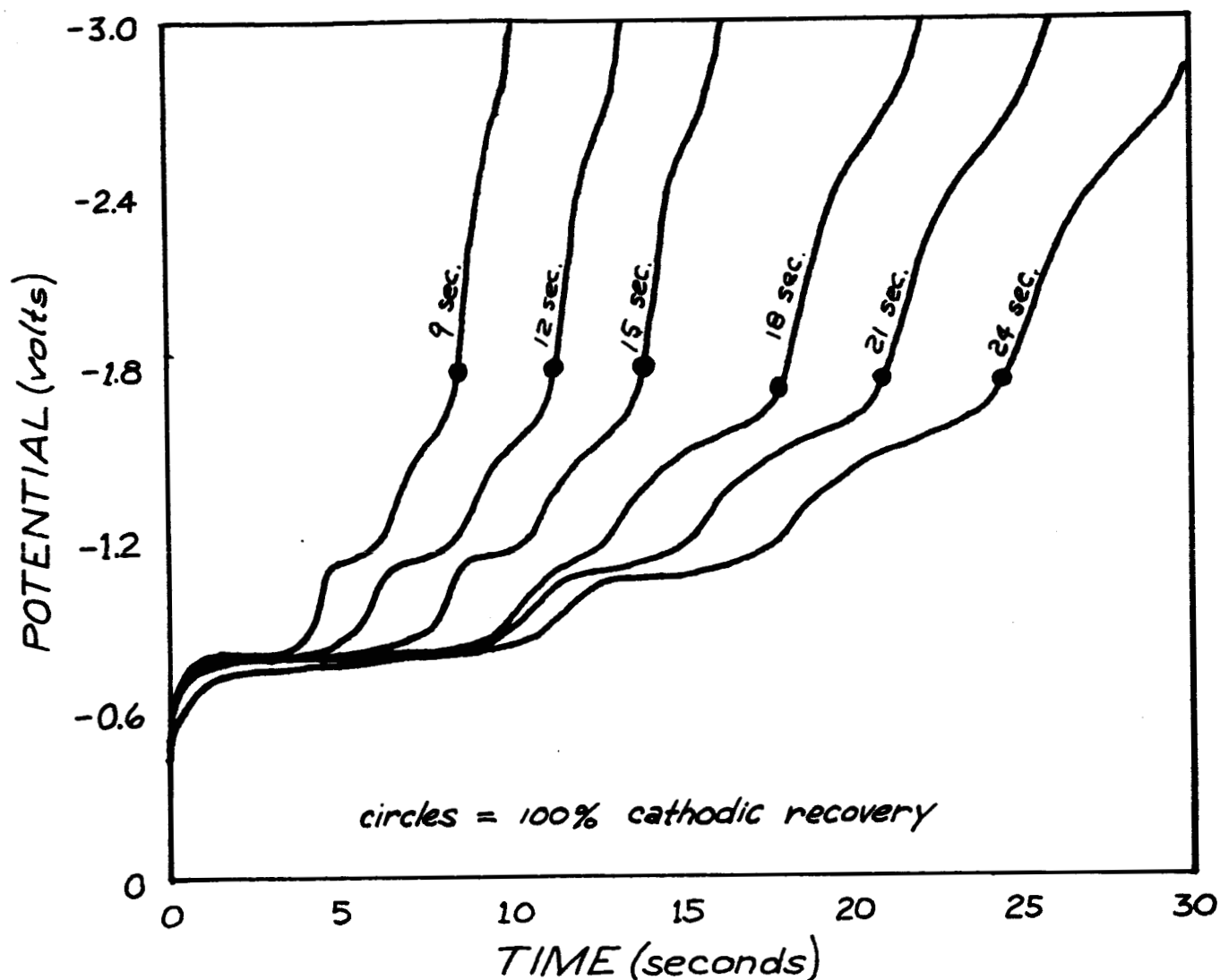


Figure 9 Constant current cathodic charging curves obtained on previously anodized polished copper electrodes in propylene carbonate, 1 M in  $\text{LiClO}_4$  and 0.1 M in  $\text{AlCl}_3$ . Initial anodizations were conducted at  $4.25 \text{ mA cm}^{-2}$  for 9, 12, 15, 18, 21, and 24 seconds respectively, but the anodic charging curves are not here shown. Anodization for the stated time was followed by immediate current reversal, and the resultant cathodic charging curves are shown in the figure. The curves are labelled according to the time previous anodization was continued. Electrode reactions are the anodic oxidation of copper to a chloride salt, followed by reduction of the salt to metallic copper.

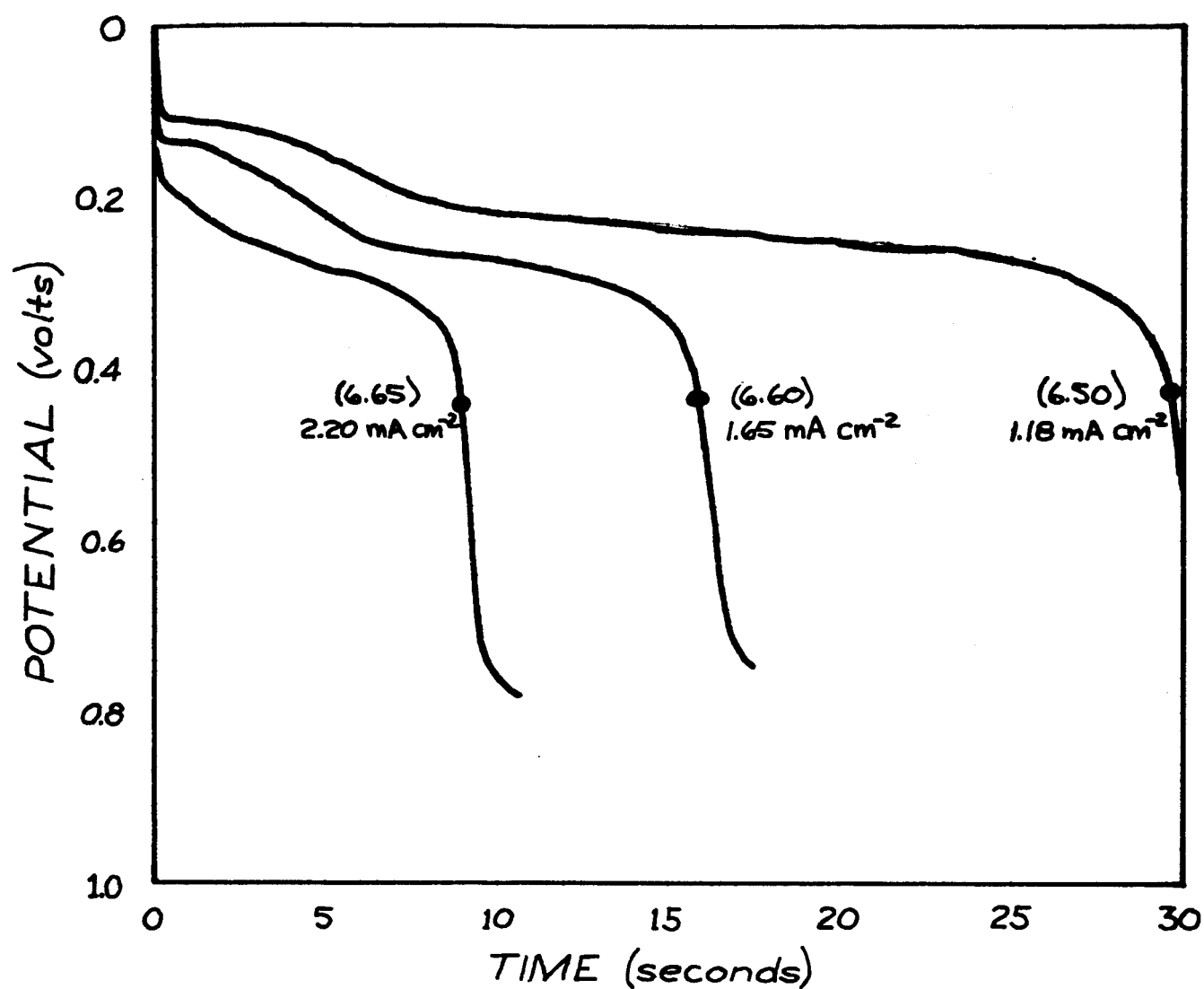


Figure 10 Constant current anodic charging curves obtained on polished silver electrodes in propylene carbonate, 1 M in  $\text{LiClO}_4$  and 0.025 M in  $\text{AlCl}_3$ . The products,  $iT^{1/2}$  in  $\text{mA cm}^{-2} \text{sec}^{1/2}$  given in parentheses are calculated using the transition times indicated by the solid circles. The anodic reaction is the oxidation of silver to an insoluble chloride.